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REACTIONS OF DIAZOACETATES with PHOSPHATE TRIESTERS and THIOPHOSPHATE TRIESTER: $\geq\overset{+}{P}\text{-}O\text{-}\overset{-}{C}<$ and $\geq\overset{+}{P}\text{-}S\text{-}\overset{-}{C}<$ INTERMEDIACY FORMATION

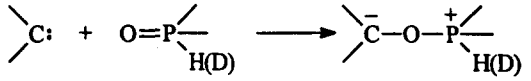
Konstantin A. Popov, Alexander M. Polozov* and Sergei V. Tcherezov

A.M.Butlerov Research Chemical Institute,

Kazan State University, Lenin Str. 18, Kazan 420008, RUSSIAN FEDERATION

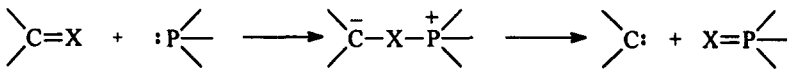
Abstract: Diazoacetates **1a,b** undergo $BF_3 \cdot OEt_2$ catalyzed carbenoid attack on the oxygen of the phosphoryl double bond of phosphate triesters **2a-c** or on the sulfur of thiophosphoryl double bond of thiophosphate **9** to form corresponding O-alkoxycarbonylmethylphosphates **3a-c** or S-alkoxycarbonylmethylphosphate **13**.

The reactions of carbenes or carbenoids with the carbon-oxygen double bond give synthetically valuable intermediate carbonyl ylides.[1,2] Surprisingly, that little is known about analogous reaction of diazo precursors with the phosphoryl-oxygen or phosphoryl-sulfur double bond. Recently, the anomaly low H/D isotope effect was found in the reaction of thermally generated fluorenyl carbene with dimethyl hydrogen phosphite indicating the carbene attack on the oxygen of P=O bond (Scheme 1).[3]



Scheme 1

It is interesting that fragmentation of the similar zwitterionic intermediate to carbene is often involved into a possible mechanism of the reactions of ketones or thioketones with tervalent phosphorus compounds (Scheme 2).[4-6]



Scheme 2

Diazo esters **1a,b** and trialkylphosphates **2a-c** were first to be chosen for intermolecular generation of zwitterionic intermediate. On slow (2 h) dropwise addition of a solution of diazo ester **1a,b** (5 mmol) in CH_2Cl_2 (10 ml) to a stirred boiling solution of catalyst (0.5 mmol) and trialkylphosphate **2a-c** (12.5 mmol) in CH_2Cl_2 (10 ml) (Scheme 3) followed by water-Na_2CO_3 work-up and $MgSO_4$ drying O-alkoxycarbonylphosphates **3a-c**[7] have been isolated by distillation.

$BF_3 \cdot OEt_2$ is the catalyst of choice what indicates a Lewis acid promoted process. It is often that $BF_3 \cdot OEt_2$ is a superior catalyst in the typical carbenoid transformations.[8]